ADDENDUM TO “ELECTRIC RESONANCE OF ROTATING DIPOLES IN IONIC CRYSTALS”

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A recently published paper by Feher, Shepherd, and Shore[1] on the electric resonance effect in KCl:KOH expressed disagreement with our previously published[2] experimental results and their interpretation. *Actually, Refs. 1 and 2 differ only with respect to the identification of the two resonance lines observed with 9-kMc/sec microwave equipment.*

Our original experimental results[2] are in reasonable agreement with these of Fig. 3 of Ref. 1. The differences in the electric field position of the peaks of the resonance lines can be attributed to the small clamping strain ($\sim 4 \times 10^{-5}$) used in Ref. 2 for the 0.1-ppm samples, and line-shape distortions due to saturation effects (at “high” microwave power levels). These differences are resolved with more refined experimental techniques.[3] The important point is that, in both 9-kMc/sec experiments, two very similar resonance peaks are observed.

Attention must now be focused on additional evidence which gives the correct identification of the transitions and thereby brings the two papers into agreement. The peak observed by Feher *et al.* at 4 kV/cm [see their Fig. 3(a)] is now recognized[4] as *not* representing the $1A_1 \rightarrow 3A_1$ transition. However, this peak also cannot result from the $1A_1 \rightarrow 2A_1$ transition as is suggested in the Erratum (Ref. 4). The reason for this has been brought out by us. Namely, this same ~4-kV/cm line (labeled LE$_z$ by us) decreases in magnitude under an applied stress in a [001] direction but its peak position remains fixed with respect to applied electric fields. In terms of Fig. 3 of Ref. 2, or alternatively in terms of an extrapolation of Fig. 2(a) of Ref. 1, one sees that the properties of LE$_z$ line are *matched only* by the properties of the $2A_1 \rightarrow 3A_1$ transition. Since only two and not three peaks are observed in the 9-kMc/sec work, the corresponding value of Δ is $3 < \Delta < 9$ kMc/sec.[5] This range for Δ brackets the value proposed by Feher, Shepherd, and Shore.[1] On this basis, the 9.1-kMc/sec work of Feher, Shepherd, and Shore is seen to agree with both their own 35-kMc/sec results and our work at the lower frequency.

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[1] G. Feher, I. W. Shepherd, and H. B. Shore, Phys. Rev. Letters 16, 500 (1966).

[2] W. E. Bron and R. W. Dreyfus, Phys. Rev. Letters 16, 165 (1966).

[3] A paper on these details will be published.

[4] G. Feher, I. W. Shepherd, and H. B. Shore, Phys. Rev. Letters 16, 1187(E) (1966).

[5] Cf. Fig. 2(a) of Ref. 1.

F_3^+ CENTER IN NaF †

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Stress splitting and polarization of the 5456-Å zero-phonon line in irradiated NaF suggest that this line and its mirror absorption and emission bands are due to the predicted $^1A_1 \longleftrightarrow {}^1E$ transition of the F_3^+ center.

The F_3^+ center in irradiated alkali halides consists of three adjacent negative-ion vacancies forming an equilateral traingle in a (111) plane with two trapped electrons. A zero-phonon line and broad absorption band in several alkali halides have been tentatively attributed to such a center on the basis of photochemical conversion and bleaching studies.[1,2] However, there are conflicting reports for the luminescence and stress behavior of the center.[2-4] In this Letter we report piezo-optical studies for the corresponding line in NaF and show, using calculations for the analogous H_3^+ molecule ion, that the results support the F_3^+ assignment.

The absorption, emission, and excitation spectra for the center in NaF are shown in Fig. 1 for a Harshaw crystal at 4°K after pro-

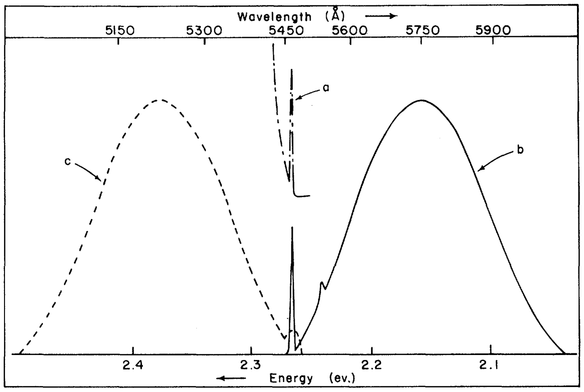

FIG. 1. Optical spectra of the $F_3{}^+$ center in NaF at 4°K. Curve (a): absorption spectrum of the 5456-Å zero-phonon line. Curve (b): emission spectrum for excitation at ~0.52 μ. Curve (c): excitation spectrum for emission at ~0.57 μ.

longed x irradiation at room temperature. The intensity of the "resonance" line at 5456 Å and the shape and spacing of the "mirror" bands imply that the most probable number of phonons involved in the transition is about five.[5] The spectral position of the line is close to that predicted for the $F_3{}^+$ center on the basis of an empirical Mollwo-Ivey plot,[2] and its formation and bleaching behavior resemble those reported by Farge, Toulouse, and Lambert[2] for the 4874-Å line in LiF.

The trigonal symmetry of the $F_3{}^+$ center implies either orbital singlet-A or doublet-E electronic states. A simple estimate of the lowest one-electron states with these symmetries made up from linear combinations of three F-center ground states suggests that an A state lies lowest with an E state next above it. If we place two electrons in these levels according to the Pauli principle, then the ground state of the center is ${}^1A_1$ and the low-lying excited states are ${}^3E_1$, ${}^1E$, and ${}^3A_2$. The only allowed dipole transition from the ground state is to the ${}^1E$ state for light polarized perpendicular to the [111] symmetry axis of the center. There should also be transitions to higher lying states made up from F-center excited states.

These are just the symmetries of the low-lying states of the analogous $H_3{}^+$ ion, and the ordering is based on an LCAO (linear combination of atomic orbitals) calculation by Hirschfelder[6] for the $H_3{}^+$. The energy-level spacing in the $F_3{}^+$ center can be estimated roughly by appropriate scaling of his results. Silsbee[7] has shown that this scaling procedure gives surprisingly good agreement in the case of the R-center (F_3) observations and H_3 calculations. We assume that the vacancy separation, in units of the effective Bohr radius for the F center, is nearly constant for the alkali halides since both the spatial extent of the F-electron wave function and the size of the $F_3{}^+$ traingle scale with the lattice parameter. Taking the value $R/a_0 \simeq 2.8$ determined for KCl,[7] the relative energies of $H_3{}^+$ and H_3 transitions can be computed from Hirschfelder's curves. The ${}^1A_1 \rightarrow {}^1E$ transition energy for the $F_3{}^+$ should be about $\frac{3}{4}$ of the ${}^2E \rightarrow {}^2A_2$ energy for the R_2 transition. Using the known R_2 band positions, $F_3{}^+$ absorption bands are predicted at ~0.50 μ in LiF, ~0.59 μ in NaF, ~0.97 μ in KCl, and ~1.07 μ in KBr, in fair agreement with the observed positions at 0.47 μ,[2] 0.53 μ, 0.96 μ,[1] and 1.02 μ,[1] respectively. A recent calculation by Wang[8] for KCl would place the $F_3{}^+$ band at 0.90 μ.

To test our assignment of $F_3{}^+$, we have studied the stress spectrum of this center in absorption and emission. The effect of applied uniaxial stress will be to lift the orientational degeneracy of these anisotropic centers, and also to split the orbitally degenerate E states. The strain coupling for an E state, discussed previously,[7,9] should cause the zero-phonon absorption line to split into two, three, and four components under [100], [111], and [110] stress, respectively, with definite predictions from symmetry for the relative intensity, polarization, and energy shift of each component. We have measured these quantities for the 5456-Å absorption line at 4°K under uniaxial stress and hydrostatic pressure and find good agreement with the predictions for an $A \rightarrow E$ transition. No other symmetry assignment appears to fit the data.

The lack of stress-induced dichroism in absorption indicates that the ground state is nondegenerate, as expected. To verify that the excited state is degenerate, we have studied the zero-phonon line in emission under [100] stress at 4.2°K, and find the stress-induced polarization shown in Fig. 2(a). This is due to a preferential population of the lower stress-split E state favoring emission polarized perpendicular to the stress axis. The dashed line indicates the intensity ratio expected from the [100] stress splitting of 0.7 ± 0.2 cm^{-1}/(kg/mm^2) measured directly in absorption. The

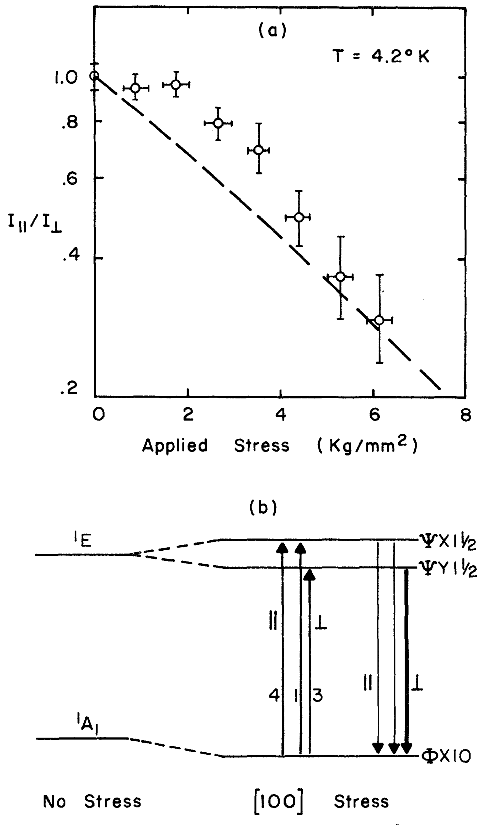

FIG. 2. (a) Ratio of the 5456-Å emission-line intensity polarized parallel to the stress to that polarized perpendicular to the stress, for stress applied in the [100] direction. The dashed line indicates the expected stress dependence, neglecting the effect of residual strains. (b) Schematic energy-level diagram for the F_3^+ center under [100] stress, with the relative strengths of the transitions in absorption. The notation for the vibronic states is that of Ref. 7.

deviation at low stress, which also occurs at 1.8 and 8°K, is probably due to residual stresses in the crystal.

The orbital degeneracy of the ^1E excited state of the F_3^+ model implies the possibility of a Jahn-Teller effect, with distortions of E symmetry removing the degeneracy of the electronic state. This effect would appear as a different stress-induced polarization for the broadband emission, resulting from modified selection rules for these vibronic states, as discussed by Silsbee.[7] The behavior of the broad band is different, and the limiting polarization ratio does appear to be close to the expected value of $\frac{2}{5}$ for a [100] stress. On the basis of these results, the stress-split states involved in the zero-phonon transition are identified with particular vibronic states in Fig. 2(b), using Silsbee's notation.

A search for transitions to higher excited states is in progress. The F_3^+ luminescence can be excited by illumination in the R band, as noted by Baumann, Von der Osten, and Waidelich[4] for LiF, but this is not a consequence of a higher transition. Instead, it is a consequence of radiative transfer from the R center to the F_3^+ center, since the R emission band at 0.54 μ lies under the F_3^+ absorption band. This luminescence trapping is most obvious when illumination and emission occur at opposite faces of the crystal.

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